This article was downloaded by: On: *25 January 2011* Access details: *Access Details: Free Access* Publisher *Taylor & Francis* Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information: http://www.informaworld.com/smpp/title~content=t713926090

Synthesis and physical properties of novel liquid crystal oligomers possessing polar terminal groups

Atsushi Yoshizawa^a; Shota Chiba^a; Fumitaka Ogasawara^b

^a Department of Frontier Materials Chemistry, Faculty of Science and Technology, Hirosaki University, Hirosaki 036-8561, Japan ^b Tohoku Chemical Corporation, Hirosaki 036-8655, Japan

To cite this Article Yoshizawa, Atsushi , Chiba, Shota and Ogasawara, Fumitaka(2007) 'Synthesis and physical properties of novel liquid crystal oligomers possessing polar terminal groups', Liquid Crystals, 34: 3, 373 — 379 To link to this Article: DOI: 10.1080/02678290601111440 URL: http://dx.doi.org/10.1080/02678290601111440

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doese should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.



Synthesis and physical properties of novel liquid crystal oligomers possessing polar terminal groups

ATSUSHI YOSHIZAWA*†, SHOTA CHIBA† and FUMITAKA OGASAWARA‡

[†]Department of Frontier Materials Chemistry, Faculty of Science and Technology, Hirosaki University, 3 Bunkyocho, Hirosaki 036-8561, Japan

[‡]Tohoku Chemical Corporation, 1-3-1, Kanda, Hirosaki 036-8655, Japan

(Received 17 August 2006; accepted 7 October 2006)

A homologous series of novel liquid crystal oligomers possessing 4-fluorobiphenyl and 4trifluoromethoxyphenyl benzoate moieties was prepared and the physical properties investigated. The dimesogenic compounds, 4-trifluoromethoxyphenyl 4-{6-[4-(4-fluorophenyl)phenyloxy]alkoxy} benzoates, exhibited nematic (N) and smectic A (SmA) phases. Pronounced odd–even effects were seen, not only for the phase transition but also for the induced dielectric anisotropy in the N phase of the mixture with a host material, on varying the spacer length of the dimeric compounds. The λ -shaped trimesogenic compound, 4trifluoromethoxyphenyl 3,4-bis{6-[4-(4-fluorophenyl)phenyloxy]benzoate, was found to show monotropic N and SmA phases. We discuss oligomeric effects of the mesogenic moieties on the phase transition behaviour, and on the induced dielectric anisotropy.

1. Introduction

Supramolecular assemblies composed of oligomeric liquid crystals are current topics in the design of liquid crystalline materials [1]. Liquid crystal oligomers consist of semi-rigid mesogenic units connected by flexible spacers [2-4]. Dimeric liquid crystals are of interest because they exhibit different properties from the corresponding low molar mass mesogens. For example, the transition properties of dimeric liquid crystals are known to depend on the length and parity of the flexible spacer. Liquid crystal trimers [5] and tetramers [6] have also been reported. Pronounced odd-even effects have been observed in the transition properties of linear liquid crystal oligomers of varying spacer length; the transition behaviour is interpreted in terms of the average molecular shape of those oligomers. U-shaped liquid crystals have been investigated by several research groups [7-10]. Attard and Douglass reported property-structure correlations of bimesogenic compounds derived from phthalic acid, providing important understanding about the U-shaped liquid crystal system [10]. In the banana-shaped 1, 3-benzene derivatives first synthesized by Matsunaga et al. [11], antiferroelectric and ferroelectric properties have recently been found by Watanabe *et al.* [12, 13]. The banana-shaped system has provided new concepts for chirality and phase structures in liquid crystals [14, 15].

We have designed several novel pre-organized systems: a flexible dimesogenic compound [16], a U-shaped molecule [17], a binaphthyl derivative [18], a λ -shaped molecule [19], V-shaped [20], T-shaped [21] and Yshaped molecules [22]; these pre-organized supermolecules were found to induce unusual ordering in the supramolecular liquid crystalline phase. We recently reported that some U-shaped compounds induce large dielectric anisotropy in their nematic mixtures and reduce the threshold voltage [23, 24]. We prepared the corresponding linear-shaped compounds with a flexible spacer and investigated the effect of spacer length on the physical properties [24, 25]. However none of the linear-shaped compounds showed any liquid crystalline phase; and we obtained no information on the relationship between dielectric anisotropy and linear molecular shape of the compounds in the nematic phase, or in the nematic mixture with a host material.

We report here the synthesis and physical properties of novel liquid crystal oligomers (figure 1) possessing 4fluorobiphenyl and 4-trifluoromethoxybenzoate moieties, and discuss oligomeric effects of the mesogenic moieties on the phase transition behaviour, and on the induced dielectric anisotropy.

^{*}Corresponding author. Email: ayoshiza@cc.hirosaki-u.ac.jp



U-shaped compound



Linear-shaped compound

Figure 1. Molecular structures of the U-shaped and linear-shaped compounds with a flexible spacer.

2. Experimental

2.1. Preparation of Materials

Purification of the final product was carried out using column chromatography over silica gel (63–210µm) (Kanto Chemical Co., Inc.) using a toluene/ethyl acetate mixture as the eluant, followed by recrystallization from ethanol. The structure of the final product was elucidated using infrared (IR) spectroscopy (FTS-30; Bio-Rad Laboratories, Inc.) and proton nuclear magnetic resonance spectroscopy (JNM-GX270, JEOL; or JNM-A400, JEOL). Elemental analysis (EA, 1110; CE Instruments) was obtained for each final compound.

2.1.1. 4-Trifluoromethoxyphenyl 3,4-bis{6-[4-(4-fluorophenyl)phenyloxy]hexyloxy}benzoate, V-(6, 6). Potassium carbonate (0.97 g, 7 mmol) was added to a solution of 1, 6-dibromohexane (2.21 g, 9 mmol) and 4-fluoro-4'-hydroxybiphenyl (1.32 g, 7 mmol) in cyclohexanone (20 ml). The reaction mixture was stirred at 80° C for 5 h. After filtration of the precipitate, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with toluene/hexane (6/4). 4-(6-Bromohexyloxy)-4'-fluorobiphenyl (1) was obtained; yield 0.62 g (25%).

Compound 1 (2.0 g, 5.7 mmol) and ethyl 3,4-dihydroxybenzoate (0.49 g, 2.7 mmol) were dissolved in cyclohexanone (20 ml). K_2CO_3 (0.79 g, 5.7 mmol) and KI (0.05 g, 0.5 mmol) were added and the resulting mixture stirred at 120°C for 9 h. The reaction mixture was filtered and the solvent removed by evaporation under reduced pressure. The product was purified by column chromatography using a toluene/ethylacetate (9/1) mixture as eluant. Ethyl 3,4-bis{6-[4-(4-fluorophenyl)phenyloxy]hexyloxy}benzoate (2) was obtained; yield 1.66 g (86%). Compound 2 (1.64 g, 2.3 mmol) was added to a solution of KOH (0.63 g, 11.3 mmol) in a water/ethanol (1/9) mixture (170 ml). The resulting mixture was stirred under reflux for 7 h, and the solution acidified with HCl. The aqueous phase was extracted with dichloromethane (600 ml), and the organic extracts evaporated. 3,4-Bis{6-[4-(4-fluorophenyl)phenyloxy]hexyloxy} benzoic acid (3) was obtained; yield 1.19 g (75%).

To a solution of compound 3 (0.65 g, 0.9 mmol)in dichloromethane (20 ml), 4-trifluoromethoxyphenol N.N'-dicyclohexylcarbodiimide (0.17 g, 0.9 mmol), (0.2 g, 1 mmol), and 4-(N,N-dimethylamino)pyridine (0.01 g, 0.1 mmol) were added. The resulting solution was stirred at room temperature for 8h. Precipitated materials were removed by filtration, and the solvent by evaporation removed. The residue was purified by column chromatography on silica gel by using a toluene/ethyl acetate (20/1) mixture as eluant. Recrystallization from ethanol gave the desired product **V-(6,6)**; yield 0.48 g (47%). ¹H NMR (400 MHz, solvent CDCl₃, standard TMS) $\delta_{\rm H}$ /ppm: 7.84(d, 1H, Ar–H, J=8.3 Hz), 7.68(s, 1H, Ar-H), 7.51-7.44(m, 8H, Ar-H), 7.31–7.24(m, 4H, Ar–H). 7.10(dd, 4H, Ar–H, J=8.8 Hz, J=8.8 Hz), 6.98–6.94(m, 5H, Ar–H), 4.15(t, 2H, Ar– OCH₂-, J=7.1 Hz), 4.12(t, 2H, Ar-OCH₂-, J=7.1 Hz), 4.02(t, 2H, Ar-OCH₂-, J=6.6 Hz), 4.01(t, 2H, Ar-OCH₂-, J=6.4 Hz), 1.96-1.61(m, 16H, aliphatic-H). IR (KBr) v_{max} /cm⁻¹: 2940, 2867, 1731, 1602, 1499, 1430, 1183, 1143. EA: calc. for C₅₀H₄₇F₅O₇, C 70.25; found, C 70.17%.

The other compounds presented in this paper were obtained by a similar method to that for compound V-(6, 6).

2.1.2. 4-Trifluoromethoxyphenyl 4-{6-[4-(4-fluorophenyl)phenyloxy]hexyloxy}benzoate, **III-6.** ¹H NMR (270 MHz, solvent CDCl₃, standard TMS) $\delta_{\rm H}$ / ppm: 8.12(d, 2H, Ar–H, *J*=8.8 Hz), 7.51–7.43(m, 4H, Ar–H), 7.25–7.21(m, 4H, Ar–H). 7.08(dd, 2H, Ar–H, *J*=8.8 Hz, *J*=8.8 Hz), 6.97(d, 2H, Ar–H, *J*=8.4 Hz), 6.95(d, 2H, Ar–H, *J*=8.6 Hz), 4.07(t, 2H, Ar–OCH₂–, *J*=6.8 Hz), 4.02(t, 2H, Ar–OCH₂–, *J*=6.6 Hz), 1.88–1.58(m, 8H, aliphatic–H). IR (KBr) $v_{\rm max}/\rm{cm}^{-1}$: 2940, 2861, 1733, 1607, 1501, 1430, 1165, 1083. EA: calc. for C₃₂H₂₈F₄O₅, C 67.60; found C 67.88%.

2.1.3. 4-Trifluoromethoxyphenyl 3-{6-[4-(4-fluorophenyl)phenyloxy]hexyloxy}benzoate, **IV-6.** ¹H NMR (400 MHz, solvent CDCl₃, standard TMS) $\delta_{\rm H}/$ ppm: 7.76(d, 1H, Ar–H, *J*=7.8 Hz), 7.67(s, 1H, Ar–H), 7.49–7.38(m, 5H, Ar–H), 7.28–7.21(m, 4H, Ar–H), 7.17(d, 1H, Ar–H, *J*=7.8 Hz), 7.08(dd, 2H, Ar–H, *J*=8.8 Hz, *J*=8.8 Hz), 6.94(d, 2H, Ar–H, *J*=8.8 Hz),

4.04(t, 2H, Ar–OCH₂–, J=6.3 Hz), 4.00(t, 2H, Ar–OCH₂–, J=6.6 Hz), 1.87–1.53(m, 8H, aliphatic–H). IR (KBr) v_{max} /cm⁻¹: 2945, 2873, 1731, 1603, 1501, 1445, 1161. EA: calc. for C₃₂H₂₈F₄O₅, C 67.60; found C 67.44%.

2.1.4. 4-Cyanophenyl 3,4-bis{6-[4-(4-fluorophenyl)phenyloxy]hexyloxy}benzoate, VI-(6,6). ¹H NMR (400 MHz, solvent CDCl₃, standard TMS) $\delta_{\rm H}$ /ppm: 7.83(d, 1H, Ar–H, *J*=8.6 Hz), 7.75(d, 2H, Ar–H, *J*=8.8 Hz), 7.66(s, 1H, Ar–H), 7.51–7.44(m, 8H, Ar– H), 7.37(d, 2H, Ar–H, *J*=8.8 Hz), 7.10(dd, 4H, Ar–H, *J*=8.6 Hz, *J*=8.6 Hz), 6.98–6.94(m, 5H, Ar–H), 4.14(t, 2H, Ar–OCH₂–, *J*=4.9 Hz), 4.10(t, 2H, Ar–OCH₂–, *J*=4.9 Hz), 4.02(t, 2H, Ar–OCH₂–, *J*=6.4 Hz), 4.01(t, 2H, Ar–OCH₂–, *J*=6.6 Hz), 1.94–1.59(m, 16H, aliphatic–H); IR (KBr) $v_{\rm max}$ /cm⁻¹: 2940, 2864, 2229, 1730, 1602, 1499, 1431, 1164, 1142. EA: calc. for C₅₀H₄₇F₂NO₆, C 75.45; found C 75.17%.

2.2. Physical properties

The initial assignments and corresponding transition temperatures for the final products were determined by thermal optical microscopy using a Nikon Optiphoto POL polarizing microscope equipped with a Mettler FP82 microfurnace and FP80 control unit. The heating and cooling rates were 5° Cmin⁻¹, unless otherwise indicated. Temperatures and enthalpies of transition were investigated by differential scanning calorimetry (DSC) using a Seiko DSC 6200 calorimeter. The compounds were studied at a scanning rate of 5° Cmin⁻¹, for both heating and cooling cycles, after encapsulation in aluminum pans. Dielectric measurements were performed using an impedance analyser (HP 4284A; Hewlett Packard Co.) with a temperature control unit at a frequency of 1 kHz [26]. A sample was contained in a homogeneous configuration cell $(5.0 \,\mu\text{m})$ where the inner surfaces had been coated with



V-(n, n)

Figure 2. Molecular structures of liquid crystalline oligomers possessing fluoro groups.

polyimide aligning agent and buffed unidirectionally (E. H. C. Co., Ltd). The dielectric measurements were performed using the single cell method and carried out three times at each measured value. The experimental error was within $\pm 0.7\%$.

3. Results and discussion

3.1. Phase transition properties

Figure 2 shows the molecular structures of the newly prepared oligomeric compounds and the corresponding monomeric compounds. Table 1 gives the temperatures and enthalpies of transition for these compounds, determined by optical microscopy and DSC.

Table 1. Transition temperatures (°C) on cooling and enthalpies $(kJ mol^{-1})$ of transition (in brackets) for compounds under investigation.

Compound	Cryst	SmX ^a	SmA	Ν	Ι	m.p.
Ι	• 36		 81 (5.84) 		•	56
II	• 77				•	78
III-6	• 90		 125 (1.02) 	 153 (5.48) 	•	130
III-7	• 46	• 63 ^b	• 64 ^b	• 105 (1.27)	•	98
III-8	• 106		• 135 (2.76)	• 141 (5.80)	•	140
IV-6	• 58		. ,		•	106
V-(6,6)	• 98		 119 (5.58) 	 129 (8.95) 	•	152
V-(7,7)	• 88				•	135

^aSmX: unidentified smectic phase. ^bThe N–SmA and SmA–SmX transitions occurred simultaneously. The total value of both transition enthalpies was 2.96 kJ mol⁻¹.

The monomeric compound I exhibited an enantiotropic SmA phase whereas compound II showed no liquid crystalline phase [24]. The dimesogenic compounds III-6, III-7 and III-8 in which 4-fluorobiphenyl and 4-trifluoromethoxyphenyl benzoate moieties are connected via a flexible spacer were found to show N and SmA phases, and compound III-7 exhibited a higher ordered unidentified smectic phase below the SmA phase. Pronounced odd-even effects are seen for the I-N and N-SmA transition temperatures of the dimesogenic compounds. The entropy changes, $\Delta S/R$, for the I-N transition of compounds III-6, III-7 and III-8 were 1.55, 0.40 and 1.69, respectively. Imrie and Luckhurst give the following interpretation for oddeven effects on the transition properties of dimesogenic compounds [2]. In the isotropic phase approximately half the conformers of an even-membered dimer are essentially linear whereas for an odd-membered dimer just 10% are linear. There exists a synergy between conformational and orientational order, and hence at the transition to the nematic phase for even-membered dimers many of the bent conformers are converted to a linear form. This enhances the orientational order of the nematic phase resulting in a larger nematic-isotropic entropy than would be expected for a monomer. For odd-membered dimers, however, the difference in free energy between the bent and linear conformers is such that the orientational order of the nematic phase is insufficient to convert bent into linear conformers. Hence, the orientational order is not enhanced and a smaller nematic-isotropic entropy would be expected.

The marked odd-even effects for the I-N transition properties of compounds III-6, III-7 and III-8 are consistent with the above interpretation. Compound IV-6, which is thought to form a bent structure, did not show a liquid crystalline phase. The λ -shaped compound V-(6,6), in which compounds III-6 and IV-6 are incorporated, exhibited monotropic N and SmA phases, on the other hand, compound V-(7,7) with oddmembered spacers did not show a liquid crystalline phase. In order to investigate the effect of the terminal polar group, we prepared compound VI-(6,6) that has a cyano group instead of the trifluoromethoxy group of compound V-(6,6). The molecular structure and transition temperatures are shown in figure 3. Compound VI-(6,6) exhibited exclusively nematic behaviour, which is attributed to intermolecular antiparallel interactions between the cyanophenyl moieties.

3.2. Dielectric anisotropy

We used 4-cyanophenyl 6-octyloxynapthalene 2-carboxylate (host A) as a host material to investigate the dielectric anisotropy of the oligomeric compounds



VI recryst 112 N 141 (7.3) Iso mp 148

Figure 3. Molecular structure, transition temperatures (°C) on cooling and enthalpies $(kJ \text{ mol}^{-1})$ of transition in brackets for compound **VI-(6,6)**.

(figure 4). The transition temperature, the parallel and perpendicular components of the dielectric constant, and the dielectric anisotropy of a mixture consisting of host A and 10 wt % of each added compound are listed in table 2. For comparison, those values induced by an equimolar mixture of the monomeric compounds I and II are also shown.

The liquid crystal oligomers were found to induce smaller values of $\Delta \varepsilon$ in the mixture than the corresponding monomeric compounds or the equimolar mixture. This behaviour was also observed for the previously reported dimesogenic system [25]. Dielectric anisotropy induced by compound III-6 or III-8 in the mixture with host A is smaller than that of host A, whereas that induced by compound III-7 is larger. Extrapolated values of compounds III-6 and III-7 from the observed $\Delta \varepsilon$ at $T_{\rm IN}$ -20°C in the mixture with host A are +4.1 and +14.7, respectively. On the other hand, observed values at $T_{\rm IN}$ -20°C of those compounds III-6 and III-7 in their N phases were +1.9 and +2.1, respectively. Odd-even effects are seen for the extrapolated $\Delta \varepsilon$ values of those compounds; however, the effects are not seen for the observed $\Delta \varepsilon$ values. There is a marked difference in $\Delta \varepsilon$ of compound III-7 between the extrapolated and observed values.

Odd–even effects are seen for the $T_{\rm IN}$ of the mixtures, indicating that there is significant difference in molecular shape between compounds III-6 and III-7 in their mixtures. As discussed above, if we assume an all-*trans* conformation for the spacer of those compounds, the two mesogenic units of compound III-6 are almost parallel, but those of compound III-7 are not. Compound IV-6, which is thought to have a more bent structure than compound III-7. The λ -shaped compound V-(6,6) was found to induce larger $\Delta \varepsilon$ in



Figure 4. Molecular structure of host A.

Table 2. Transition temperature (°C), parallel component $(\varepsilon_{l/})$ and perpendicular component (ε_{\perp}) of dielectric constant,^a and dielectric anisotropy ($\Delta \varepsilon$) of a mixture consisting of host **A** and 10 wt % of each compound.

Compound	$T_{\rm IN}$	8//	ϵ_{\perp}	$\Delta \varepsilon$
Host A	135	19.3	7.4	11.9
Ι	124	20.4	7.4	13.0
II	124	19.2	7.1	12.1
I-II mixture ^b	119	19.2	6.9	12.3
III-6	135	18.1	7.0	11.1
III-7	128	18.9	6.7	12.2
III-8	132	18.8	7.1	11.7
IV-6	114	20.6	8.0	12.6
V-(6,6)	128	18.9	7.0	11.9

^aDielectric measurements were performed at T_{IN} -20°C with a frequency of 1 kHz. ^bI-II mixture: an equimolar mixture of compounds I and II.

the mixture than III-6 but a smaller $\Delta \varepsilon$ than compound IV-6. The λ -shaped compound VI-(6,6), possessing a – CN group, induced 11.9 of $\Delta \varepsilon$ at $T_{\rm IN}$ -20°C in the N phase of the mixture. The $\Delta \varepsilon$ induced by compound VI-(6,6) is the same as that induced by compound V-(6,6).

The dielectric anisotropy of a uniaxial liquid crystalline phase can be described as

$$\Delta \varepsilon = (NhFS)(\varepsilon_0)^{-1} \left[\Delta \alpha - \mu^2 F (2k_{\rm B}T)^{-1} (1 - 3\cos^2\beta) \right] (1)$$

where *F* and *h* are the reaction field and cavity field factors that account for the field-dependent interaction of a molecule with its environment, *N* is the number density, *S* is the order parameter, μ is the dipole moment, $\Delta \alpha$ is the molecular polarizability anisotropy, and β is the angle between the dipole moment vector and the effective orientation axis of the liquid crystal molecule [27].[†]

First we discuss the values of $\Delta \varepsilon$ induced by each dimesogenic compound in its N phase, which are smaller than those induced by the monomeric compounds. Figure 5 shows a molecular organization model for the N phase consisting of compound **III-6** and host **A**. Directions of the C–OCF3 and C–F of compound **III-6** are almost inverse within a single molecule, which results in a small $\Delta \alpha$. Thus the dimesogenic compounds induced smaller values of $\Delta \varepsilon$ than did the corresponding monomeric compounds.

The larger $\Delta \varepsilon$ induced by compound III-7 than that by compound III-6 is attributed to an increase in the



Figure 5. A possible model for molecular organization of a mixture consisting of **III-6** and host **A**.

parallel component of the dielectric constant. The significant large $\Delta \varepsilon$ induced by compound **IV-6** can also result from a marked increase of the parallel component of the dielectric constant. The increase of the parallel component may result from an increase in the effective dipole moment of the system, i.e. the dipole moment along the director that constitutes the coupling between μ and β . Thus, the large $\Delta \varepsilon$ induced by compounds **III-7** or **IV-6** is interpreted in terms of conformational change, in that compounds **III-7** and **IV-6** form not a bent structure, but an almost U-shaped structure in host **A** as shown in figure 6 [24].

There is another possible reason for the increase of $\Delta \varepsilon$. Our previous studies on a homologous series of linear-shaped compounds, the ∞ -(4-trifluoromethoxyphenyloxy)- ω -[4-(4-fluorophenyl)phenyloxy]alkanes (see figure 1, n=6-12), showed that the compounds with a longer central spacer (n=11, 12) only induced larger $\Delta \varepsilon$ in the mixture with 6OCB [25]. These results indicate that only the linear-shaped compounds with a long and flexible spacer can form a U-shaped conformation. It seems to be difficult for compounds **III-7** and **IV-6** to form such a U-shaped structure, because the spacer length is too short for the conformation. Furthermore, if compound **III-7** formed



Figure 6. A molecular conformation model for compound **III-7** in host **A**.

[†] In equation (1), *F* denotes the reaction field factor $[F=1/(1-f\alpha); f=(\varepsilon-1)/2\pi\varepsilon a^3(2\varepsilon+1)]$, and *h* the cavity factor $[h=3\varepsilon/(2\varepsilon+1)]$. The macroscopic dielectric constant is used for ε .



Figure 7. A possible model for the effect of molecular biaxiality on organization of the host molecules.

a U-shaped structure, the induced value of $\Delta \varepsilon$ should be much larger than that induced by the monomeric compound [25]. The alternative explanation for the increase of $\Delta \varepsilon$ is that the bent-formed dimesogenic compound can affect the organization of the host molecules in the nematic mixture, which results in an increase of $\Delta \varepsilon$ of the system (see figure 7). With respect to the λ -shaped compounds V-(6,6) and VI-(6,6), $\Delta \alpha$ of VI-(6,6) possessing a -CN group is thought to be larger than that of V-(6,6) possessing a -OCF₃ group; however, there is no difference between them in the induced $\Delta \varepsilon$. These results also suggest that the molecular shape of an additive plays an important role in the induced $\Delta \varepsilon$ of the mixture. Further investigation is necessary to clarify this hypothesis.

Reduced driving voltage is an important requirement for LCD improvement. Liquid crystalline materials with high dielectric anisotropy ($\Delta \epsilon$) are known to decrease the threshold voltage (V_{th}) of the electro-optical response of a dielectrically positive liquid crystal mixture. Consequently, they decrease the driving voltage of a twisted-nematic (TN) display. On the other hand, a high voltage holding ratio (VHR) of the liquid crystal is necessary for thin film transistor (TFT) LCDs. A molecule possessing a polar group, such as –CN, induces large $\Delta \epsilon$ but lowers the VHR. The present results indicate a possibility that a bent-shaped additive may increase $\Delta \epsilon$ of the nematic mixture without decreasing the VHR.

4. Conclusions

A homologous series of novel liquid crystal oligomers containing 4-fluorobiphenyl and 4-trifluoromethoxyphenyl benzoate moieties was prepared. Odd–even effects were seen for the phase transition behaviour of these dimesogenic compounds. Furthermore, a λ shaped mesogenic trimer with even-numbered spacers exhibited monotropic N and SmA phases, however, a mesogenic trimer with odd-numbered spacers did not exhibit a liquid crystalline phase. The dimesogenic compounds in which the mesogenic units are thought to be bent, were found to induce larger dielectric anisotropy in a mixture with a host nematic material, than that seen for similar compounds in which the mesogenic units are coparallel.

Acknowledgement

This work was supported by the Aomori Prefecture Collaboration of Regional Entities for the Advancement of Technological Excellence, JST.

References

- [1] (a) J.W. Goodby, G.H. Mehl, I.M. Saez, R.P. Tuffin, G. Mackenzie, R. Auzely-Velty, T. Benvegu, D. Plusquellec. *Chem. Commun.* 2057 (1998); (b) I. Saez, J.W. Goodby. J. mater. Chem., 15, 26 (2005).
- [2] C.T. Imrie, G.R. Luckhurst. In the *Handbook of Liquid Crystals* Vol 2B, D. Demus, J.W. Goodby, G.W. Gray, H.-W. Spiess, V. Vill (Eds), pp. 801–833, Wiley-VCH, Weinheim (1998).
- [3] C.T. Imrie, P.A. Henderson. Curr. Opin. colloid interface Sci., 7, 298 (2002).
- [4] C.T. Imrie. Struct. Bonding, 96, 149 (1999).
- [5] P.A. Henderson, A.G. Cook, C.T. Imrie. *Liq*, *Cryst.*, 31, 1427 and references cited therein (2004).
- [6] P.A. Henderson, C.T. Imrie. *Liq*, *Cryst.*, **32**, 1531 and references cited therein (2005).
- [7] D. Vorländer, A. Apel. Chem. Ber., 65, 1101 (1932).
- [8] H. Matsuzaki, Y. Matsunaga. Liq. Cryst., 14, 105 (1993).
- [9] T. Kato, H. Adachi, A. Fujishima, J.M.J. Frechet. *Chem.*, *Lett.*, 265 (1992).
- [10] G.S. Attard, A.G. Douglass. Liq. Cryst., 22, 349 (1997).
- [11] T. Akutagawa, Y. Matsunaga, K. Yasuhara. *Liq. Cryst.*, 17, 659 (1994).
- [12] T. Niori, T. Sekine, J. Watanabe, T. Furukawa, H. Takezoe. J. mater. Chem., 6, 1231 (1996).
- [13] E. Gorecka, D. Pociecha, F. Araoka, D.R. Link, M. Nakata, J. Thisayukta, Y. Takanishi, K. Ishikawa, J. Watanabe, H. Takezoe. *Phys. Rev. E*, **62**, R4524 (2000).
- [14] D.R. Link, G. Natale, R. Shao, J.E. Maclennan, N.A. Clark, E. Karblova, D.M. Walba. *Science*, **278**, 1924 (1997).
- [15] G. Pelzl, S. Diele, W. Weissflog. Adv. Mater., 11, 707 (1999).
- [16] (a) A. Yoshizawa, N. Ise, T. Okada. Ferroelectrics, 214, 75 (1998); (b) A. Yoshizawa, K. Yamamoto, H. Dewa, I. Nishiyama, H. Yokoyama. J. mater. Chem., 13, 172 (2003); (c) A. Yoshizawa, M. Kurauchi, M. Kohama,

H. Dewa, K. Yamamoto, I. Nishiyama, T. Yamamoto, J. Yamamoto, H. Yokoyama. *Liq. Cryst.*, **33**, 611 (2006).

- [17] A. Yoshizawa, A. Yamaguchi. Chem. Commun., 2060 (2002).
- [18] (a) J. Rokunohe, A. Yoshizawa. J. mater. Chem., 15, 275 (2005); (b) J. Rokunohe, A. Yamaguchi, A. Yoshizawa. Liq. Cryst., 32, 207 (2005).
- [19] A. Yamaguchi, I. Nishiyama, J. Yamamoto, H. Yokoyama, A. Yoshizawa. J. mater. Chem., 15, 280 (2005).
- [20] A. Yoshizawa, H. Kinbara, T. Narumi, A. Yamaguchi, H. Dewa. *Liq. Cryst.*, **32**, 1175 (2005).
- [21] A. Yoshizawa, M. Sato, J. Rokunohe. J. mater. Chem., 15, 3285 (2005).

- [22] A. Yoshizawa, M. Nakata, A. Yamaguchi. Liq. Cryst., 33, 605 (2006).
- [23] A. Yoshizawa, F. Ogasawara, K. Manabe, S. Segawa, T. Narumi. Jpn. J. appl. Phys., 43, L1549 (2004).
- [24] A. Yoshizawa, S. Segawa, F. Ogasawara. Chem. Mater., 17, 6442 (2005).
- [25] A. Yoshizawa, J. Rokunohe, S. Segawa, F. Ogasawara. Proc. SPIE, 6135, 613508 (2006).
- [26] T. Uchida, Y. Takahashi. Mol. Cryst. liq. Cryst., 72, 133 (1981).
- [27] (a) W. Maier, G. Meier. Z. Naturforsch. A, 16, 262 (1961); (b) D. Dunmur, K. Toriyama. Handbook of Liquid Crystals Vol 1, D. Demus, J. W. Goodby, G. W. Gray, H.-W. Spiess, V. Vill. (Eds), pp. 231–252, Wiley-VCH, Weinheim (1998).